UNITED STATES PATENT APPLICATION

For

METHODS AND APPARATUS FOR CYCLE TIME IMPROVEMENTS FOR ATOMIC LAYER DEPOSITION

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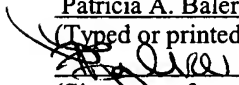
Methods and Apparatus for Cycle Time Improvements for Atomic Layer Deposition

RELATED APPLICATION

[0001]   This application is related to and hereby claims the priority benefit of U.S. Provisional Patent Application No. 60/455,034, entitled "Method and Apparatus for Cycle Time Improvement for ALD", filed 03/14/2003 assigned to the assignee of the present application and incorporated herein by reference.

FIELD OF THE INVENTION

[0002]   The present invention relates to thin film processing and, more particularly, to methods and apparatus for improvement in the cycle time of Atomic Layer Deposition (ALD) processes.

BACKGROUND

[0003]   In the field of material deposition, a process known as atomic layer deposition (ALD) has emerged as a promising candidate to extend the abilities of chemical vapor deposition (CVD) techniques. Generally ALD is a process wherein conventional CVD processes are divided into individual, sequential deposition steps that theoretically achieve saturation (and exhibit self-limited growth) at the level of a single molecular or atomic layer thickness. After each deposition step, unreacted chemical precursors used therein (and the unwanted byproducts of the reaction) must be removed from the reactor chamber. Existing techniques for doing so include the so-called "pump" or "evacuation" method and the "purge" or "flow" method. Of these, the purge or flow procedures have become the method of choice for commercial operation of ALD reactors because the efficiency of precursor removal by purge is improved over that provided by evacuation. See, e.g., M.

Ritala and M. Leskela, "Deposition and Processing" in Handbook of Thin Film Materials, H.S. Nalwa (ed.), Vol. 1, Ch. 2 (2002).

[0004]   In the purge or flow method, chemical molecular precursors are introduced separately into a reactor. Typically, each precursor exposure is followed by an inert gas purge to assist in the removal of the extra reactive precursor chemicals from the reactor just prior to the introduction of the next precursor. This sequence of steps may be repeated several times to provide for the complete formation of a desired material film. The total time to carry out the series of sequential steps or "periods" of: (i) exposure of precursor A, (ii) inert or neutral gas purge (for removal of unreacted precursor A), (iii) exposure of precursor B, and (iv) inert or neutral gas purge (for removal of unreacted precursor B), is called the "cycle time" (CT). The above 4 periods are called expose period of A, purge period of A, expose period of B, and purge period of B, respectively. The time period that consists of expose period of A and the following purge period of A is called half cycle A. Similarly, the time period that consists of expose period of B and the following purge period of B is called half cycle B.

[0005]   To provide for greater wafer throughput, it is a goal of semiconductor manufacturers to reduce the CT of ALD processes. Many pulse/purge times are reported in the literature and it is commonly found that the purge times are long relative to the exposure pulse times. This is particularly true when very good film uniformity over large area substrates is desired. Thus, in the current state of the art, it is generally the purge component(s) of ALD cycles that provide(s) the limiting factors on the CT. Indeed, a typical case may utilize purge times 1.5 – 5 times longer than the exposure times. Note that this is true even in the case of plasma-assisted ALD processes in which only a single purge process is required. See, e.g., U.S. Patent 6,200,893 of Sneh, assigned to the assignee of the present invention.

[0006]   To provide for the desired increase in wafer throughput then, cycle time reductions, and in particular purge time reductions, are needed. One way in which this can be accomplished is to provide an increased flow for the purge gas. Providing the purge gas at a higher flow rate will tend to minimize the time needed to complete the purge period. However, given conventional ALD reactor designs (which utilize constant purge gas flow rates and strive to maintain constant reactor chamber pressures using a downstream throttle valve), this would tend to increase the required precursor exposure time. This is because the increased flow rate of the purge gas (which is used as a neutral carrier during the exposure periods) would tend to drive the chemical precursors out of the reactor chamber faster than would otherwise be the case at a lower purge gas flow rate. Hence, a greater loss of chemical precursor for a unit time interval could be expected and so increased exposure times would be necessary.

[0007]   To avoid this situation, a bi-level purge gas flow rate could be implemented. That is, during precursor exposure a relatively low purge gas flow rate could be used (to maximize precursor residence time within the chamber) whereas during the purge period a relatively high purge gas flow rate could be used (to minimize the required purge time). The first known system to implement such a bi-level purge gas flow rate was developed in 1998 by Steven Shatas for Modular Process Technology of San Jose, CA ("MPT"). Later, in 1999, Shatas and MPT (working with one of its customers) combined the use of a bi-level purge gas flow driven by a pair of mass flow controllers with a fast-switching throttle valve downstream from the reactor chamber to permit control of both flow rate and reactor pressure. This system allowed operators to vary the residence time of the precursors during the ALD cycle, providing low residence time during precursor removal and high residence time during exposure.

[0008]   More recently, a bi-level flow system using a purge bypass into a draw chamber (located downstream of the reactor chamber) during precursor exposure has been described by Sneh. See O. Sneh, WO 03/062490 A2, "ALD Apparatus and Method" (July 31, 2003). In this so-called "synchronously modulated flow draw" (SMFD) process, a high flow rate through the reactor chamber is maintained during purge, but a low flow rate is used during deposition. The low flow rate is achieved by dumping a significant portion of the purge gas into the downstream draw chamber via a reactor bypass conduit. Thus, only a portion of the purge gas flow finds its way to the reactor chamber during the deposition sequence and so the chemical precursors are allowed to remain therein for a sufficient residence time.

[0009]   Both the Shatas and Sneh systems for providing bi- or multi- level flows suffer from deficiencies. In the Shatas system, the dual purge source was provided using mass flow control components. These components are limited in their speed of response and also require ancillary flow (dumping) of the neutral purge gas during the period when the source is not injected into the reactor. This makes for relatively inefficient use of purge gas. Similarly, in the Sneh SMFD device the purge source bypasses the reactor during exposure, but the purge gas is always flowing at a high rate from its source. This tends to waste purge gas. Hence, new methods and apparatus for reducing the purge time while maintaining adequate precursor residence times are needed.

SUMMARY OF THE INVENTION

[0010]   In one embodiment, the present invention provides for performing an expose period (which may, in some cases, be a plasma-assisted period) of an ALD process using a first purge flow and a first pumping capacity, and performing a purge period of the ALD process using a second purge flow greater than the first purge flow and a second pumping capacity greater than the first pumping capacity. These procedures may be performed while maintaining the reactor chamber within which the ALD process is performed at a nominally constant pressure, for example through the operation of a throttle valve downstream from the reactor chamber such that the throttle valve is more open during the purge period than during the expose period. The first purge flow and the second purge flow may, in some cases, utilize different gasses and/or may be provided through different flow paths.

[0011]   In some cases, the second purge flow and second pumping capacity may be initiated prior to termination of material deposition during the expose period. Alternatively, or in addition, the second purge flow and second pumping capacity may be activated so as to break turbulence within the reactor chamber (e.g., to help in the removal of precursors). Also, a second expose period of the ALD process may be performed using a third purge flow and a third pumping capacity different from the first purge flow and first pumping capacity, respectively. In some cases, the third purge flow may be an absence of a purge flow.

[0012]   In various embodiments, the first purge flow may be switched to the second purge flow: at a substantially coincident point in time as the first pumping capacity is switched to the second pumping capacity, prior to completion of material deposition during the expose period, or at a different point in time than that at which the first pumping capacity is switched to the second pumping capacity. In some cases, the purge flows may

be switched by switching first flow limiting conductances located upstream of the reactor chamber out of a first gas flow path thereto at a substantially coincident point in time as second flow limiting conductances located downstream of the reactor chamber are switched out of a second gas flow path from the reactor chamber.

[0013]   In still further embodiments, the present invention allows for performing, within a half cycle, an expose period of an ALD process using a first purge flow defined in part by a first conductance of an annular gas flow pathway within the reactor chamber, and performing a purge period of the ALD process using a second purge flow greater than the first purge flow, the second purge flow defined in part by a second conductance of the annular gas flow pathway within the reactor chamber. The pressure of the reactor chamber may be maintained so as to be nominally constant during the expose and purge period, and in some cases, the first purge flow and the second purge flow may utilize different gasses and/or be provided through different flow paths.

[0014]   Still further embodiments of the present invention provide for performing an expose period of an ALD process using a first purge flow at a first pressure, the first purge flow passing through first flow limiting conductances located within a first gas flow pathway upstream of the reactor chamber and second flow limiting conductances located within a second gas flow pathway downstream of the reactor chamber, and performing a purge period of the ALD process using a second purge flow at a second pressure greater than the first pressure, the second purge flow passing through third flow limiting conductances located within the first gas flow pathway and fourth flow limiting conductances located in the second gas flow pathway, wherein a ratio of the first flow limiting conductances to the second flow limiting conductances is equal to a ratio of the third flow limiting conductances to the fourth flow limiting conductances and a pressure of the reactor chamber is maintained nominally constant during the ALD process.

[0015] Another embodiment provides an ALD system that includes a first purge flow pathway coupled upstream of a reactor; a second purge flow pathway coupled upstream of the reactor; and a pumping arrangement coupled downstream of the reactor, and configured to be switched between a first pumping capacity when the first purge flow pathway is active and a second pumping capacity greater than the first pumping capacity when the second purge flow pathway is active. The first and second purge flow pathways may share a common gas flow manifold with one or more precursor injection pathways, or at least one of the purge flow pathways may be directly coupled to the reactor independently of the other. In some cases, the first and second pumping capacities comprise two operational modes of a single physical pump.

[0016] Additional embodiments of the present invention provide an ALD system having a purge flow pathway coupled upstream of a reactor chamber through selectable upstream flow limiting conductances having two or more operational modes including a low flow mode and a high flow mode; and a pumping arrangement coupled downstream of the reactor through selectable downstream flow limiting conductances having two or more operational modes including a low flow mode and a high flow mode, wherein the upstream flow limiting conductances and downstream flow limiting conductances are configured to switch operational modes in time-phase with one another. The upstream flow limiting conductances may be configured to switch operational modes prior to the downstream flow limiting conductances switching operational modes. In some cases, the downstream flow limiting conductances include a throttle valve, which may be an annular throttle valve located within the reactor chamber.

[0017] Still further embodiments of the present invention provide an ALD system that includes a gas delivery system coupled to a reactor chamber having disposed therein an annular throttle valve positioned within a gas flow pathway from the reactor chamber to a

pumping system coupled downstream of the reactor chamber. The annular throttle valve may have two or more operating modes, each configured to provide a different flow path conductance from the reactor chamber.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018]   The present invention is illustrated by way of example, and not limitation, in the figures of the accompanying drawings in which:

[0019]   Figure 1 illustrates a conventional ALD processing apparatus having a split-flow gas manifold.

[0020]   Figure 2 illustrates conventional (idealized) baseline conditions for ALD reactor operation at constant pressure and flow.

[0021]   Figure 3A is a graph that illustrates variations in ALD reactor flows due to the introduction of chemical precursors.

[0022]   Figure 3B is a graph illustrating the effects of chemical precursor introduction on ALD reactor pressures.

[0023]   Figure 4 illustrates an ALD processing apparatus configured with a two-level purge source and dual pump capacity arrangement in accordance with an embodiment of the present invention.

[0024]   Figure 5 illustrates the use of a direct-coupled purge flow conduit in accordance with a further embodiment of the present invention.

[0025]   Figure 6 illustrates an ALD apparatus configured to provide for multi-level purge flows through the use of tracking conductances in accordance with yet another embodiment of the present invention.

[0026]   Figure 7 illustrates an ALD apparatus configured for tracking conductance operation using a direct-coupled purge gas conduit in accordance with another embodiment of the present invention.

[0027]   Figure 8 illustrates an ALD apparatus configured with an annular throttle valve in accordance with still another embodiment of the present inventions.

[0028]   Figure 9 illustrates various examples of annular throttle valves for use in accordance with embodiments of the present invention.

[0029]   For ease of reference, reference numerals in the accompanying drawings typically are in the form "drawing number" followed by two digits, xx; for example, reference numerals on Figure 4 may be numbered 4xx; on Figure 5, reference numerals may be numbered 5xx, and so on. In certain cases, a reference numeral may be introduced on one drawing and the same reference numeral (with a different drawing number indicator) may be utilized on other drawings to refer to the same item.

DETAILED DESCRIPTION

[0030]   Described herein are methods and systems for cycle time improvements in ALD processes. In various embodiments, the present invention provides multi-level flow sources using pressure controlled and/or passive conductance components combined with a dual (or, more generally multiple) pump (or dual or multiple pump capacity) arrangement. Unlike the multi-level flow systems described above, in the present invention a high purge flow does not have to flow during the exposure pulse, resulting in more economical operation with respect to consumables usage. Both lower cost and better dynamic time-dependent performance is obtained, in some embodiments, by the use of pressure controlled components instead of mass flow controllers. Further, in some embodiments the use of an independent, direct-coupled conduit for neutral gas flow, instead of a purge bypass, provides multi-level purge source capability without the need for continual operation of a high purge flow.

[0031]   In addition to reduced consumables consumption, another benefit afforded by the two or multiple level flow purge operation of the present invention is better step coverage. To achieve better step coverage, higher exposure (defined as partial pressure multiplied by exposure time) is needed. By limiting the pumping rate and the dilution of the precursor, the present invention assures that more precursor molecules reach the extremes of high aspect ratio/high topology structures and/or the bottom of trenches in a given expose period.

[0032]   It should be remembered that the various embodiments described herein are intended merely to illustrate systems and methods incorporating the present invention and are not to limit the overall scope of the invention. The principle of time-phased, multi-level flow to vary residence time during ALD processes may described in terms of a method for varying flows and also controlling pressure over the ALD cycle and there are

many different ways to implement the procedure. For example, in the case of no limiting constraints, such as operation at non-constant reactor chamber pressure, an ideal sequence may be:

i) Close by command (or move toward the closed position) a downstream throttle valve during reactant exposure time. This allows the precursor to reside a sufficiently long enough time in the chamber to achieve substantially about or more than 99% completion of the saturating ALD half-reaction.

ii) Remove the extra precursor as quickly as possible. This may be done by driving the purge gas flow rate to higher values during the purge period by the switching action using an upstream higher-pressure level source.

Where, however, the reactor chamber pressure is to be constrained at a nominally constant pressure, the present invention allows for the same by maintaining the throttle valve less open at low flow rates during reactant exposure and more open at high flow rates during purge. Further, because an ALD half-reaction for a first precursor (A) may be very different from that for a second precursor (B), the flow rates during the A cycle and the B cycle may be different. To accommodate the need for varying exposure flow rates due to different precursor requirements, the present invention provides for a "multi-value" or multi-level" flow rate, consisting of two or more flow levels.

[0033]   In general then the present invention provides systems and methods that provide low flow levels concurrently matched to low pumping capacities during exposure times and high flow levels concurrently matched with higher pumping capacities during purge times. Other cycle time improvement techniques that are known in the art, such as those due to chemical delivery assistance using flow controllers or pressure controlled methods (see, e.g., U.S. Patent 6,503,330, assigned to the assignee of the present invention and incorporated herein by reference), or ALD precursors delivered from "charge tubes"

(see, e.g., Gadgil et al., WO0079019) or pressurized precursor volumes may be used in conjunction with the present methods and apparatus.

[0034]   Before describing embodiments of the present invention in detail it is helpful to present some background regarding state of the art ALD reactor design. This will provide readers unfamiliar with the technology sufficient basis to better appreciate the present invention. Thus, we refer first to **Figure 1**, which shows an ALD processing system 100 and is adapted from the above-cited U.S. Patent of the present assignee.

[0035]   ALD processing system 100 includes a split-flow gas switching manifold 102, through which a neutral purge gas (from source 104) and one or more chemical sources (or process gasses) 106 and 108 may be delivered to reactor chamber 110. Neutral carrier gases may or may not accompany the chemical precursor. Within the chamber 110 is a heater assembly 112, upon which rests a semiconductor wafer 114. When both shut-off valves 116 and 118 are closed, and neutral purge gas flows through the reactor 110, baseline purge flow and pressure conditions are established. In general, the split-flow manifold can include one or more inject conduits to the reactor 110; and system 100 is illustrated with a dual inject.

[0036]   Prior to precursor injection, the flows and pressure in the reactor 110 are determined by: the upstream pressure setting at purge gas source 104, the pressure setting at the reactor chamber 110 and the operation of the downstream throttle valve 120. The throttle valve 120 is part of a closed loop, feedback control system 122, which operates to keep the pressure in the reactor chamber constant (or nearly so) as the various chemical precursors are introduced into the reactor 110. Various "restrictors" and conduit conductance limitations as may be useful may be placed in the gas switching manifold 102 (e.g., in reactor purge pathways 126 and 124), but are not shown in detail. Where used such restrictors and conductances may also determine the quantitative pressure and flow

values. Overall though, the split-flow architecture provides a nominally constant gas pressure and (continuous) flow background for ALD operation, as illustrated in **Figure 2**.

[0037] Using a neutral carrier gas (that is distinct from the purge gas) precursor injections are carried out to move the precursor chemicals into the purge stream. That is, precursors are introduced to the purge stream from their respective sources 106, 108 via valves 116 and 118, respectively. This is done alternately and sequentially in time.

[0038] The condition for the injection into the purge stream at valve 116 (or 118) is established by the pressure value set just above the upstream position of valve 116 (or 118) by controller 117 (119). This allows precursor injection or blending into the purge gas stream on either side of the manifold 102. At the input 128 to the chamber, the two precursor lines open below the entrance to the reactor (forming multi-injects).

[0039] Once the flows of the carrier with precursor join the baseline purge flow, the overall flow in the reactor 110 will increase. If the carrier flow is small relative to the purge, which may be (and often is) the case, the increase in total flow and increase in reactor pressure will be small, but nevertheless observable, as shown in **Figure 3A**. One reason for this pressure rise above the baseline value may be that the response time of the throttle valve 120 is long compared with that of the injection valves 116, 118. That is, the inertia of the throttle valve 120 may lead to fluctuations in the reactor pressure during the purge period. Typical response times for injection valves 116 and 118 may be on the order of 20 – 30 msec, whereas response times of a typical downstream throttle valve 120 may be on the order of 500 – 1000 msec (though throttle valves having response times of less than 100 msec have recently become available). Thus, the pressure in the reactor 110 may rise in coincidence with the increased flow.

[0040] In fact, the pressure in the reactor 110 may change and fluctuate above and below that of the baseline flow level both during and after the period of the exposure pulse

as shown in **Figure 3B**. Typically, the total reactor pressure is maintained during the middle and towards the end of the purge half-cycle, where the precursor's partial pressure is low enough to start the other precursor injection, because the throttle valve 120 and its closed-loop control system 122 have corrected to reestablish the desired reactor pressure. A well-designed system will exhibit a smooth decay of pressure vs. time.

[0041] Having thus described a state of the art ALD processing system, we turn now to a discussion of the present invention. As indicated above, the present invention makes use of a time-phased, multi-level flow to vary precursor residence time during ALD processes. Residence time is defined as the time it takes for a molecule of a reactant gas to move through a space (e.g., the reactor chamber) with a certain volume. If the pressure of the reactant gas is p, the volume of the space is V, and the flow rate is F, then the residence time r.t. is given by $r.t. = pV/F$. For example, if $p = 200$ mTorr ($0.2/760$ Atm), $V = 1000$ cm^3, $F = 200$ sccm (3.33 cm^3/sec), then r.t. $= 0.079$ sec $= 79$ msec. Alternatively, or in addition, residence time may be expressed in terms of the reactor volume (V) and the effective pumping speed (S) at the orifice where the precursor is removed from that volume: $r.t. \sim V/S$.

[0042] During reactant exposure times (a.k.a. pulse times, which, historically, have been of the order of or greater than a few hundred msec), it is desirable to have long residence time (e.g., to conformally coat high aspect ratio devices). Since the reactor chamber volume and pressure are relatively constant, and the residence time is inversely proportional to the flow rate, in order to achieve longer residence time, lower flow rate is necessary. However, long residence time is not desirable during the reactant removal time (purge time) because a longer residence time means a longer purge time. In order to achieve shorter residence time, higher flow rate is necessary. Therefore, there is a conflict between the needs of reactant exposure and reactant removal.

[0043]   The present invention's use of a time-phased, multi-level flow overcomes this conflict by using different purge flow rates so that residence time of reactant molecules can be optimized in different periods of an ALD cycle. By doing so the overall ALD cycle time is reduced (over that required by conventional systems), allowing for greater wafer throughput. Importantly, the present invention achieves this advantage while at the same time not requiring the use of a continual, high flow purge which tends to be wasteful. Indeed, if the purge flow were simply increased over the entire ALD cycle, then the precursor would be driven out of the reactor chamber too fast during the exposure times and this adversely increases the exposure time. By using a relatively low flow rate during precursor exposure the present invention may, in some embodiments, actually allow for shortening the pulse time further helping to decrease the overall ALD cycle time.

[0044]   In addition to using time-phased, multi-level flow, some embodiments of the present invention utilize different purge gasses during the different ALD half-cycles. That is, a different purge gas may be used during the purge period than is used during the exposure period. To understand the rationale for this use of different purge gasses, consider the following. The collision theory of hard sphere may be used to estimate the number of collisions per unit volume per unit time for the purge gas "P" on the precursor "A" or "B." See, e.g., K.J. Laidler, Chemical Kinetics, pp. 81-87 (1987). For two unlike molecules, the collision rate is:

$$N_P \times N_A \times r^2 \times (kT/m^*)^{1/2}.$$

Here N_P is the concentration of purge gas, N_A the concentration of precursor gas "A" and m^* is the effective mass ($m_A m_p / m_A + m_p$) of the purge and precursor molecules. This indicates that a higher concentration of purge gas density increases the collision rate and increases the forward momentum for removing the precursor gas. Although the collision rate is higher as the effective mass is lowered by $1/\sqrt{m^*}$, the transferred momentum to the

precursor gas is linear in the mass of the neutral purge gas molecule, so the choice of purge gases favors heavier masses by the square root of $m*$. In this respect, Ar with atomic mass 40 may be more favorable than N_2 with atomic mass 28. Thus, in some embodiments of the present invention Ar is used during the purge period, while N_2 may be used as an independent control gas during the exposure period to lower gas usage costs.

[0045]   Finally, embodiments of the present invention provide for maintaining the reactor pressure nominally constant. Such a condition is desirable during ALD (and CVD) processes because it helps to keep particle contamination within the reactor chamber to a minimum. To understand why this is so, consider that all chemical deposition techniques are accompanied by parasitic deposition on the walls and surfaces of the reactor. After a certain total thickness and accumulation, the deposits flake off due to stress effects and provide secondary, macro-particle contamination. These particles may be up to microns in size (distinguishing them from much smaller, sub-micron sized particles caused by gas phase nucleation). Large variations in pressure within the reactor can result in the premature flaking off of these particles, a situation that aggravates the maintenance of the deposition reactor. Although there is no well-defined range over which reactor pressure must controlled in CVD or ALD processes, an empirically defined range of operational pressures acceptable for film deposition suggests a "substantially constant pressure" of approximately $1 - 3$ times the baseline operating pressure may be suitable, but variations of pressure greater than five times the baseline pressure may be unsuitable (though in some cases such operation may be desirable to break turbulence that helps to eliminate precursors that may have become trapped in the reactor chamber).

[0046]   In one embodiment of the present invention then, an ALD reactor is controlled at a nominally constant pressure using a closed loop feedback controlled, or a command controlled open loop downstream throttle valve. By maintaining an acceptable,

substantially constant pressure for the reactor, secondary, macro-particle contamination is minimized. If the flow rate of the purge gas is rapidly reduced to a low value, the throttle valve will move (at least initially) to a more closed position, which results in a longer residence time for the precursor in the reaction chamber. This is desirable during the pulse time, but undesirable during the purge time. Consequently, the present invention incorporates a bi- or multi- level purge flow capability in addition to the throttle valve. If two purge flow levels (low and high) are used, the low purge flow is used during the exposure pulse (allowing for a relative increase the precursor exposure and increased chemisorption and chemical utilization in a given time) and the high purge flow is used during the purge (to reduce residence time of the residual precursor), providing an advantageous situation for both the exposure and purge half-cycles.

[0047] More generally, the present invention provides several alternative embodiments for the operation of time-phased, multi-level flow (TMF) ALD processes. One such method includes the use of two or more downstream pumps (or pump capacities if a single pump is used), switched substantially in time-phase with two or more upstream purge flows (e.g., between low and high levels). This method may be used in either of two modes: mode I, without the second pump (pump capacity) to allow longer residence time during a lower flow level purge; or mode II, with the second pump (or pump capacity) switched on during the higher flow level purge. The pressure can be maintained nominally constant if the higher-level flow is matched to the pumping capacity of the combined pumps (or higher pumping capacity if a single pump is used).

[0048] In a second method, the purge flow is controlled by switching upstream, flow-limiting conductances (e.g., from a low to a high value for low and high flow, respectively) in time-phase with downstream conductances (e.g., from a low to a high level for low and high flow, respectively). This method is referred to herein as "tracking conductance(s)" in

the system. This approach provides not only the ability to keep the pressure of the reactor nominally constant (as long as the fraction of upstream and downstream conductances are the same at any point in time during the switching cycle), but also allows for a wide dynamic range of purge flows. The upstream switching conductances may be placed in a variety of configurations: for example, in series with or imbedded within a split-flow chemical manifold, or in parallel with the chemical delivery manifold lines. The downstream switching conductances may also be placed in a variety of positions: for example, in the locale of the first downstream constriction just downstream from the reaction zone, or integrated as part of the downstream throttle valve (which in this case is controlled independently so as to assume designed positions or openings and is not used in a closed loop control mode).

[0049]   In a third method, a separate purge gas control line (which may also be called a direct-coupled conduit or DCC) independent of the chemical sourcing in the split-flow manifold, is fed into the reactor pump stack either above the throttle valve or below the throttle valve, or into the first constriction leading from the reaction space. Using this path an independent control gas flow level may be set with an independent pressure regulator. The source may be an independent gas type (e.g., N_2 or He) relative to that used as the main ALD reactor purge (e.g., Ar). This independent purge gas control line may also be asynchronously timed relative to the period of the end of the exposure pulse (ahead of the period of the desired action), providing flexibility for optimizing the multi-level flows. The independent higher temperature control of this line also provides better purge capability without promoting the decomposition of precursors with low decomposition temperatures.

[0050]   Generally, the DCC may either pass parallel to the split-flow manifold, or be part of an ALD system that has all its sources directly coupled to the reactor. Thus, the

multi-level flow purge gas may pass in parallel to the chemical sourcing or serially through it. To demonstrate the idea, a second neutral-purge conduit line can be added to the apparatus with appropriate fast gas switching valve arrangements. A residual gas analyzer may be used to detect how precursor concentrations change. If the valves that control the purge lines are quite far away from the chamber, the response time may be unfavorably long (e.g., a couple of seconds). To minimize this problem valves may be placed suitably close to the chamber and /or larger diameter purge lines may be used between the upstream pressure sources and the chamber. All the controlling valves may be integrated into a common hub or block, ensuring minimal response time, as may be known in the art.

[0051]   To achieve the multi-level purge methods described above, an ALD apparatus 400 having a second purge conduit that is introduced upstream of the chemical gas switching manifold and in parallel with the first purge conduit is provided. This arrangement (which may be termed a dual flow purge manifold 403) is illustrated in **Figure 4**. Both purge sources may be pressure controlled (e.g., using pressure controllers 409 and 411) with set points of pressure that can be widely different. Given the current state of the art, the pressure controllers 409 and 411cannot be fast gas switched below several hundred milliseconds (however, future pressure controllers may allow for direct, fast electronic control). We avoid this shortcoming by passing the pressurized gas through fast switching pneumatic valves (with conductances determined by the conduit lines, elbows, valve and any restrictor components in the lines between the pressure sources 409/411 down to and including the entrance 428 to the reactor 410). This implementation has each purge conduit leading to switching valves 405 and 407. These valves may be as fast (e.g., on the order of 20 msec) as are used for precursor injection valves 416 and 418.

[0052]   Within the dual flow purge manifold 403, valve 405 may be configured to actuate below a relatively low pressure suitable for use during the exposure pulse. Valve

407, on the other hand, may be configured to actuate below a relatively high pressure, suitable for use during the purge period. The precise timing for these valves to be switched on and off may be in a range of times around 10 – 30 msec. The turn-on and turn-off times may not need to be nor want to be coincident with the turn-on and turn-off times of the exposure pulses. This allows for reliable software control for optimizing and minimizing the time between actual switchover between the exposure and purge flows within the reactor chamber 410. This is discussed further below, in developing the concept of optimal time-phased, multi-level flow using asynchronous flow concepts.

[0053]   The ALD apparatus 400 also has provision for a second pump 432 placed at a downstream location along with the first system pump 430. Pump 432 can be switched into operation by opening valve 434 at a time substantially coincident with the turn-on of the upstream, higher-pressure valve 407. The two pumps described here can be two physical pumps or two fractions of the pumping capacity of a single physical pump. The latter is referred to as virtual pump. If the conductance of valve 434 is appropriately selected the result can be the maintenance of nominally constant pressure during the entire ALD cycle.

[0054]   Operation with this two level ALD purge apparatus 400 may be carried out advantageously in many modes, some of which are illustrated in the following tables. The time elements reflected in the tables represent either a particular period, T_X, or a particular instant, t_x, in time. Graphical illustrations of these time periods and instances are reflected in Figure 3B, however, the illustration of reactor pressure in the figure is not necessarily meant to correspond to the operational conditions reflected in the tables.

[0055]   Operation Mode I: non-constant pressure. In this mode of operation (illustrated in Table 1), the downstream throttle valve 420 may be set at a fixed position: e.g., at a position corresponding to a desired reactor baseline pressure, or may be fixed as fully open (o). The switching on of the upstream higher-level pressure through valve 407

may result in excursions of pressure in the reactor chamber 410 in the time frame of the pulse-purge operations. In this mode pump 432 is not used and valve 434 is closed (c).

Table 1: Operation at Non-constant Pressure

Time:	T_1	t_2	T_3	t_4	T_5	t_6	T_7	t_8	$T_9(T_1)$	$t_{10}(t_2)$
Function:	Purge B		Expose A		Purge A		Expose B		Purge B	
Valve 416	c	o	o	c	c	c	c	c	c	o
Valve 405	c or o	o	o	c	c or o	o	o	c	c or o	o
Valve 418	c	c	c	c	c	o	o	c	c	c
Valve 407	o	c	c	o	o	c	c	o	o	c
Valve 434	c	c	c	c	c	c	c	c	c	c

[0056]   Operation Mode II: nominally constant pressure. Here, the downstream throttle valve 420 may be set to a fixed position: e.g., at a position corresponding to a desired reactor baseline pressure, or may be fixed as fully open. As illustrated in Table 2, the switching on of upstream, higher level pressures through valve 407 and the action of the downstream throttle valve 420 for switching into pump 432 via valve 434 may ensure that a correction towards or to the baseline reactor chamber pressure occurs in the time frame of the pulse-purge operations.

Table 2: Operation at Nominally Constant Pressure

Time:	T_1	t_2	T_3	t_4	T_5	t_6	T_7	t_8	$T_9(T_1)$	$t_{10}(t_2)$
Function:	Purge B		Expose A		Purge A		Expose B		Purge B	
Valve 416	c	o	o	c	c	c	c	c	c	o
Valve 405	c or o	o	o	c	c or o	o	o	c	c or o	o
Valve 418	c	c	c	c	c	o	o	c	c	c
Valve 407	o	c	c	o	o	c	c	o	o	c
Valve 434	o	c	c	o	o	c	c	o	o	c

[0057]   Additional configuration variations or combinations for different operational modes can, of course, be used. One such configuration would be the passage of inert purge gas directly to the reactor (using an appropriate timing sequence) and run in parallel to by-

pass the precursor-switching manifold 402. The flow of the additional purge gas can be increased during the purge step to provide for increase in the total flow and thus decrease the purge time. This gas can be delivered through a specially designed gas manifold for optimal purge efficiency.

[0058]   Variants on the design illustrated in Figure 4 include an ALD apparatus having a pump and connecting valve (in place of or in addition to pump 432 and valve 434) that are connected to the pump stack above the throttle valve 420. Such an arrangement may permit more efficient pumping. The valve may be a parallel array of large diameter pneumatic switching valves, or a fast switching (e.g., on the order of or less than 100 msec) throttle valve.

[0059]   Another variant includes a high flow purge source that is directly and independently connected to the rector 410. This high flow purge source would be independent of and parallel to the chemical switching manifold 402. In this case the independent purge source (which may include multiple purge flows) may be either the high or low flow, the other being the purge taken from the chemical switching manifold 402.

[0060]   With reference to the direct-coupled conduit (DCC) method described above, one embodiment of an ALD apparatus 500 implementing such a conduit is shown in **Figure 5**. Here, the conduit 536 runs in parallel to bypass the split-flow manifold 502 in a manner that allows purge switching by valve 538. This high flow purge line is independent of the main purge line through the chemical switching manifold, which can be one or both of lines from pressure sources 509 and 511. Such an independent line may be used to limit the pumping speed during the exposure downstream to affect the effective pumping speed of the pump in the reactor zone. The high flow is driven by pressure controller 540 and actuated by valve 538 during the purge. The precursor chemicals may be injected with or

without carrier gas and also with or without neutral gas from the purge, if valves 516 and 518 are closed during the exposure part of the cycle.

[0061]   In alternative embodiments, a DCC may be run from the downstream side of valve 507 (or 505) directly to the reactor 510, bypassing (or not bypassing) the split-flow route. Or, where a non-split-flow manifold is used, independent precursor conduits may feed the ALD reactor and a DCC may be run in parallel therewith. In such a case, the DCC purge may be differentiated from the other lines feeding the reactor chamber by virtue of it containing only a high level of neutral gas flow during the purge periods, and/or by its relatively large conductance to promote purging of the reactor chamber relative to the precursor feed lines.

[0062]   In still another embodiment, the DCC itself may be modified to permit two- or multi-level flow control (e.g., by replacing pressure controller 540 and valve 538 with a split- or multi-source manifold). In such an embodiment, a lower flow level via the DCC 536 may be used during exposure and a higher one during purge. In this configuration, either or both chemical precursors may be run without neutral gas dilution.

[0063]   Another embodiment, shown in **Figure 6**, may be used to implement the tracking conductances approach referred to above. In ALD apparatus 600, the upstream purge pressure is common and fixed, using pressure controller 642. By switching (e.g., via valves 644 and 646) the upstream flow through two different limiting conductances (e.g., metering valves) 648 and 650, having low and high conductance values, respectively, the overall purge flow (low or high, respectively) may be set. The low and high flows are substantially switched in time phase with the downstream conductances from a low to a high level (for low and high flow, respectively). This approach provides the ability to keep the pressure of the reactor nominally constant as long as the fraction of upstream and downstream conductances are the same at any point during the switching cycle. Certainly

this will be the case at the steady state set points of the exposure and purge periods. This solution provides both a wide dynamic range of purge flows as well as a design constrained to operate at nominally constant pressure.

[0064]   The reactor pressure for a reactor of very large conductance (compared with the conductances in line from source 642) placed in series between an upstream flow limiting conductance and downstream flow limiting conductance can be approximated by an expression for the chamber pressure:

$$P_{cham} \sim {}^{u}P \times [(1/{}^{d}C) / (1/{}^{d}C + 1/{}^{u}C)] \qquad (1),$$

where ${}^{u}P$ is the upstream pressure that may be set with a pressure controller, and ${}^{d}C$ and ${}^{u}C$ are the downstream and upstream conductances, respectively. The reciprocal conductances are proportional to the flow impedance, so at any constant flow the chamber pressure is just the ratio of pressure drop across the downstream impedance to the total impedance.

[0065]   This model is used to write Eq. 1, and is analogous to that provided by an electrical circuit, with constant supply voltage Vs (analogous to the upstream pressure), and upstream series resistance, Ru (analogous to the upstream reciprocal conductance) and node voltage below Ru (analogous to the chamber pressure), a downstream resistance (analogous to the downstream reciprocal conductance) and a ground (analogous to the downstream pump). In this linear equivalent circuit, the node voltage is given by:

$$Vs \times [Rd / (Rd + Ru)].$$

A key difference in the gas stream case is that the conductance elements may not be operating in a linear range with respect to their dependence on pressure. Nevertheless, regardless of the functional form of the pressure drop across the conductances, such a proportionality can be used.

[0066]   The upstream pressure is typically approximately several 10s to 100 Torr and the chamber pressure is approximately 100 mTorr to 1 Torr. Thus the typical impedance ratio, downstream to total, is a factor of 10 – 100. ALD apparatus configured in accordance with the present invention typically provide flow rates for ratios in a range of up to approximately 100, though in some cases higher ratio values may exist because downstream impedance may be mainly determined by the position of the throttle valve (minimum) and pump capacity (maximum).

[0067]   Considering the typical case then, the total impedance to flow must be able to be changed by a factor of approximately 100 or more. If the value of ^{d}C at its lowest value is approximately 10 l/s (downstream throttle valve near closed), the corresponding value of ^{u}C may be set by design to be approximately 0.5 l/s, providing a pressure drop of 21:1, but the flow is small and limited by the upstream restricting conductance. If the upstream pressure is 10 Torr, the chamber pressure will be 10/21 or approximately 500 mTorr and the flow is 10 x 0.5 Torr l/s. This represents the condition of the flow and pressures when the flow is in a low state.

[0068]   If the value of ^{d}C at its highest value is approximately 1000 l/s (downstream throttle valve near open), the corresponding value of ^{u}C may be judiciously set by design to be approximately 50 l/s, again providing a pressure drop of 21:1, and the flow is now large and limited by the upstream restricting conductance. If the upstream pressure is 10 Torr, the chamber pressure will again be 10/21 or approximately 500 mTorr and the flow is 10 x 50 Torr l/s. This represents the condition of the flow and pressures when the flow is in a high state, which is 100 times the low state flow.

[0069]   This example can be favorably generalized so that the pressure in the chamber remains nominally constant at all times in the ALD cycle. This can be done if the upstream

and downstream conductances have factional values of their full range, which is always the same fraction:

$$P_{cham} \sim {}^{u}P \times [(1/\,{}^{d}f\,{}^{d}C) / (1/\,{}^{d}f\,{}^{d}C + 1/\,{}^{u}f\,{}^{u}C)] \tag{2},$$

where ${}^{d}f$ and ${}^{u}f$ are the fraction of the range of conductance of the downstream and upstream conductances, respectively. If the ratio of ${}^{d}f$ to ${}^{u}f$ (call it f) is always the same at any point in time and a common fraction f of the range of the conductance of the downstream and upstream valves or restrictors, the f values cancel in the expression and the pressure is canonically constant, $P_{cham} \sim {}^{u}P \times [(1/\,{}^{d}C) / (1/\,{}^{d}C + f/\,{}^{u}C)]$.

[0070]   As illustrated in **Figure 7**, the tracking conductances approach can be implemented using a DCC 736. The DCC gas pressure level may be set with an independent pressure regulator 742 and the source may be an independent gas type (e.g., N_2 or He) relative to that used as the main ALD reactor purge (e.g., Ar) from source 752. The tracking conductances 748 and 750 may be set for low (exposure) and high (purge) flow, respectively. The switching valves, 744 and 746, may be set for low and high flows substantially coincident with the setting of the downstream conductance of the throttle valve 720 to achieve nominally constant pressure during exposure and purge.

[0071]   The matching of the ratio of upstream and downstream conductances (tracking conductances) is designed to achieve a low flow during the exposure, corresponding to high residence times, and a high flow during precursor removal or purge, for low residence times. By maintaining constant (or nearly so) the ratio of the conductances, substantially constant pressure in the reactor is achieved. An alternative method to achieve constant pressure, but still with different flows, is to use independent, directly coupled conduit lines. A first gas line may inject a purge flow at level "Fp" directly into the reaction space, and a second independent (separate) line directly coupled downstream from the reaction space may provide an appropriate flow level "Fe" to the

pump. The upstream and downstream flow values are selected so as to provide for nominally constant pressure (e.g., within a range of +/- 50% of an average) to be achieved in the reactor during the periods of purge and exposure. In the case where small flow limiting conductances exist between the downstream injection position and the reaction space, the flows may be substantially the same. The upstream purge may be selected to enhance entrainment of the precursor reactant for its removal. For example, Ar (having a relatively heavy mass) may be used to maximize the entrainment during purge. Heavier neutral gases (Kr, Xe, etc.), although more efficient as entrainment gases, are likely too expensive to use in commercial reactors. The downstream purge may be selected to reduce cost as it is not active during the purge, and N_2 is the gas of choice (He being more expensive that N_2).

[0072]   Another alternative is to route the independent gas control line to provide a flow to the pump 730 that reduces the effective pumping speed on the reaction chamber 710 during the exposure time, thus increasing the residence time of precursors therein. In such an apparatus, the DCC line 736 would be routed to the zone between the throttle valve 720 and the pump 730, rather than to the reactor 710.

[0073]   In one embodiment, ALD apparatus 700 may allow for a multi-level flow source having an upstream regulated inlet pressure of 35 Torr, leading into a split-flow manifold. The split-flow manifold may have a low flow branch set at 10 sccm as determined by a metered needle valve (e.g., type SSVR4) with a Cv of .005 - .03 and high flow branch set at 1000 sccm as determined by a metered valve (e.g., type SS-4BMRC-VCR) with a Cv of .05 to .3. The low flow branch may have a fast switching pneumatic valve (e.g., type Veriflo 955AOLP, Cv = .55) positioned upstream of the needle valve. The purge flows may be input to the reaction zone (which may be at 200 mTorr) of the reactor independently of the A and B chemical supply flow line(s). Specifically, the purge flows

may pass through a gas distribution module which has a flow coefficient (Cv) of more than 70 and which does not result in significant pressure drop, and from there through a perimeter orifice annulus (which has a Cv of more than 150) beyond the wafer perimeter to the lower part of the reactor vessel. From the reactor vessel the gas path may be to and through a restriction set by a fast switching pressure control throttle valve (e.g., type VAT 61 with a 4" throat), leading to a 6" diameter foreline to a rough pump (e.g., type BOC Edwards iH1800) that can maintain gas flows well above 2000 sccm with a reactor pressure of 200 mTorr. The controllable conductance range for the throttle valve is 1 to 1400 l/s. For such a system, a flow of 100 sccm at a reactor pressure of 200 mTorr will require a conductance of 6.3 l/s and a flow of 1000 sccm will require a conductance of 63 l/s, both well within the range of the throttle valve.

[0074]   The independent purge line provides the flexibility to optimize the minimization of exposure time. If the DCC switching is started ahead of the actuation of the exposure time by a time, dt, the effective pumping capacity at the point of the exit orifice to the reaction volume can be time-phased to be coincident with the arrival of precursor into the reaction volume. In this way, the delay of the reduced pumping speed arriving at the reaction chamber is matched with the arrival of the precursor through the upstream switching manifold. dt is given by the residence time of the precursor gas between the injecting valve and the reaction chamber and includes the conductances of connecting lines, orifices and distribution module (e.g., showerhead components). We refer to this method as asynchronous timing (AT) for optimizing the edges of the expose and removal periods in the cycle time. AT can be applied with any of the methods or apparatus of the present invention described herein.

[0075]   In still another embodiment, the tracking conductance approach may be implemented using an annular throttle valve (ATV) 854, as illustrated for the ALD

apparatus 800 shown in Figure 8. ATV 854 is used to adjust the conductance of an annular

gas flow pathway in the reactor 810 so that the gas flow rate through the reactor can be

adjusted. Recall that the residence time (r.t.) of a molecule in a space with volume V and

flow rate F is given by r.t. = pV/F. When ATV 854 is open, it provides high conductance

(i.e., high flow rate). Therefore the residence time of the reactant molecules is short. When

an ATV 854 is closed, it provides low conductance (i.e., low flow rate). Therefore the

residence time of the reactant molecules is long. Thus, by adjusting the ATV (e.g., between

a fully open position and a fully closed position, or any positions therebetween) the

residence time or the precursors can be adjusted according to different needs in exposure

time and removal time.

[0076]   This approach places a fast switching (e.g., less than or the order of 100

msec), limiting conductance as close to the reaction space as possible. This provides the

advantage of sharp residence time control, with minimal precursor backflow. That is, little

or no precursor will flow through the low conductance state of the ATV and the effect on

residence time will be felt with minimum delay.

[0077]   The ATV 854 of the present invention is a throttle valve that adjusts the

conductance of a conduit with annular cross section. An ATV's conductance can be

adjusted (e.g., opened, closed or moved to a position therebetween if more than just

discrete modes are provided) electrically, magnetically, mechanically, pneumatically or by

another method. An ATV can be adapted to any convenient opening/closing configuration,

and several examples of such configurations are shown in **Figure 9**. Each of these ATVs is

designed to provide varying conductances through an opening 958 having an annular cross-

section.

[0078]   In a first example, a wedge-shaped vane ATV 960 provides a means of

continuous conductance adjustment. This ATV has multiple wedge-shaped vanes 962, each

of which can rotate about its axis 964 (which in the illustration lies in the plane of the page). When the plane of a vane is parallel to the plane of the wafer holder (susceptor), the vane is in its fully closed position. When all of the vanes (which may be independently controlled) are in this position, the ATV 960 is in its fully closed position and the conductance of the conduit is at minimum. When the plane of a vane is perpendicular to the plane of the wafer holder, it is at its fully open position. When all of the vanes are in this position the ATV 960 is fully open and the conductance of the conduit is at maximum. By varying the number of fully open or fully closed vanes, the conductance of the conduit can be adjusted from its minimum (all vanes fully closed) to its maximum (all vanes fully open). Of course, it is possible to implement vanes that can assume positions other than fully open or fully closed so as to provide a 'fine tuning' ability in terms of regulating the conductance of the conduit. In general, a vane's weight and momentum of inertia should be minimized to allow for a fast response time.

[0079]   In a second example, a camera shutter (or iris diaphragm) ATV 966 also provides a means of continuous conductance adjustment. This ATV has multiple blades 968 that move in the plane that is nearly parallel to the plane of the susceptor. It imitates a camera shutter movement except that a camera shutter closes from a certain diameter to zero diameter position while this ATV closes from the position of the outer diameter of the ring to the position of the inner diameter of the ring. The inner diameter of the ring usually is very close to the diameter of the susceptor. The conductance of the conduit can be continuously adjusted when the blades of camera shutter ATV 966 move from a fully open position to a fully closed position.

[0080]   The third example in the illustration shows a baffle ATV 970 which allows for two-state (open & closed) operation. This ATV consists of two identical annular pieces or blades, one on top of the other, with a group of holes 972 within each of them acting as

conduits. When the holes of the two pieces coincide, gas can flow through the holes, and the ATV is said to be open. When the two pieces have an angular displacement with respect to one another such that none of the holes overlap, gas cannot flow and the ATV is said to be closed. By varying the annular displacement of the blades with respect to one another then, the conductance of the conduit can be turned on and off. If the displacement of the two blades can be controlled carefully so that the two groups of holes partly overlap with each other, the conductance can be continuously adjusted between a fully open and a fully closed state. Alternatively, or in addition, by varying the hole positions or increasing the number of blades (each possibly having different hole layouts and/or sizes) this form of ATV can be adapted to have three, four or more modes of operation, each of which will provide varying numbers (and perhaps sizes) of open holes (and, hence, varying conductance) to allow gas to pass therethrough.

[0081]   Compared to a conventional throttle valve, an annular throttle valve is closer to the wafer, which makes chamber pressure response time shorter (due to the reduced volume above the valve). It also increases the efficiency of reactant usage. Compared to the "draw control chamber" method described by Sneh, an important advantage of an annular throttle valve is that it can prevent back diffusion to the reaction zone that interferes with the precursor distribution.

[0082]   The ATV may be operated in a fashion very similar to that for the conventional throttle valve discussed above. In general, the ATV provides more efficient coupling with the upstream module that provides the time-phased multi-level flows. Table 3 illustrates some operational modes for an ATV.

Table 3: Operational Modes for ATV

	ATV position	Flow in chamber	Residence time
Exposure	Low Flow	Low	Long
Removal	High Flow	High	Short

[0083]   Thus, methods and apparatus for cycle time improvements in ALD processes have been described. In the foregoing discussion the invention has been described with respect to various illustrated embodiments thereof, however, it should be remembered that these descriptions were for convenience only and should not be read as limiting the broader scope of the invention. For example, although the methods and apparatus described above were discussed with reference to thermal ALD, they are equally applicable to plasma-assisted ALD. In such cases one of the precursors may first be exposed with no plasma, followed by a high flow level purge operation, then a plasma-assisted exposure of the second precursor may be followed by either no purge or a higher flow level purge. The benefit in cycle time improvement for the plasma-assisted process may be quantitatively less than that for the thermal ALD case because plasma-assisted ALD cycles may be run without a purge period following the plasma-assisted half-reaction. Although a plasma-assisted step at higher flow pressures may be advantageous in some applications. In addition, one may choose to operate the purge in a neutral plasma mode, if the plasma purging has no deleterious effect of the deposited film on the substrate/wafer. A suitably designed electrode configuration for use with active purging during plasma may result in a limited reaction and a better controlled surface reaction during surface precursor adsorption for improved film quality. Finally, certain variants of classical ALD developed by some of the present inventors concurrently with the methods and apparatus described herein, such as sub-saturation ALD (e.g., Transient Enhanced ALD and Starved Reaction ALD) can be further enhanced by the use of the present methods and apparatus. In these processes, the self-limiting ALD reactions are either designed to just reach the onset of saturation or not permitted to go to completion. Thus, the full scope of the present invention should be measured only in terms of the claims, which follow.